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(21) International Application Number: PCT/US97/15806 (22) International Filing Date: 4 September 1997 (04.09.97) (30) Priority Data: 60/025,512 5 September 1996 (05.09.96) US (71) Applicant: TALISON RESEARCH [US/US]; Suite 210, 1250 Oakmead Parkway, Sunnyvale, CA 94086-4027 (US). (72) Inventor: KOLLURI, Omprakash, S.; 2305 Cervantes Way, Campbell, CA 95008 (US). (74) Agent: FRANCIS, Ralph, C.; Francis Law Group, 1946 Embarcadero, Oakland, CA 94606 (US).		(81) Designated States: CA, JP, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: ULTRASONIC NOZZLE FEED FOR PLASMA DEPOSITED FILM NETWORKS (57) Abstract <p>A monomer delivery system for a chemical vapor deposition apparatus, comprising at least one ultrasonic atomizing nozzle disposed in the reactor chamber of the chemical vapor deposition apparatus for supplying a vaporized liquid monomer to said reactor chamber for depositing a film on at least one substrate contained therein, a supply vessel for storing said liquid monomer, metering means disposed between the supply vessel and atomizing nozzle for controlling the amount of liquid monomer delivered to the atomizing nozzle, and pulse damping means in communication with said metering means for providing a substantially even flow of liquid monomer at a substantially constant pressure to the atomizing nozzle.</p>		

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ULTRASONIC NOZZLE FEED FOR PLASMA DEPOSITED FILM NETWORKS

BACKGROUND OF THE INVENTION

The present invention generally relates to plasma deposited functional film
5 networks. More particularly, the invention relates to an ultrasonic nozzle system for
plasma polymerization.

It is well known that monomers which exist in a liquid or solid state at room
temperature are typically employed for depositing plasma polymerized organic or
inorganic films. Since such monomers are generally fed into the reactor as a vapor or a
10 mist for effective ionization, use of these monomers is often quite limited. In the case of
monomers which exist as liquids at room temperature, the common practice is to "bubble"
an inert carrier gas through a container holding the liquid monomer. The monomer vapor
is entrained in the carrier gas in a manner analogous to the process of humidification and
delivered to the reactor.

15 When a low boiling or high vapor pressure monomer is employed, the partial
pressure of the monomer vapor in the carrier gas is high enough to deliver sufficient
concentrations of monomer to the plasma reactor. When high boiling and/or low vapor
pressure monomer is employed, it is difficult to entrain enough monomer vapor in the
carrier gas without heating the monomer to high temperatures. This is often not possible
20 since some of the noted monomers are thermally sensitive and either degrade upon
heating or are susceptible to "runaway polymerization".

It is well known that the extent to which a monomer is vaporized and the partial
pressure of the monomer vapor are directly proportional to the monomer temperature. It
is also well known that the concentration of the monomer delivered to the reactor depends
25 on the degree of accuracy to which the temperature of the monomer can be controlled.
Since this temperature relationship is non-linear, minor fluctuations in monomer
temperature will typically produce wide variations in the amount of monomer delivered to
the reactor.

When monomers that exist as solids at room temperature are employed, additional problems are encountered. For example, condensation and subsequent solidification in the delivery lines severely restricts flow and, in many instances, shuts off the monomer supply to the reactor. In an effort to remedy this problem, heated delivery lines have been employed. However, such systems continue to be plagued with condensation problems and fluctuations in the rate of monomer delivery.

Several additional systems and techniques have also been employed to provide an effective, controlled amount of monomer to a chemical vapor deposition (CVD) reactor. Illustrative are the systems disclosed in U.S. Pat. Nos. 5,204,314 and 5,451,260. In U.S. Pat. No. 5,204,314, a system is disclosed wherein a liquid is transferred to a heated mesh for vaporization just prior to introduction into a reactor. An inert carrier gas such as argon is employed to flush the vaporization zone and transport the vapor into the reactor. As will be appreciated by one having skill in the art, when feeding thermally sensitive materials, such materials are highly susceptible to damage by virtue of the thermal exposure inherent in these devices. Therefore, when feeding monomers that thermally polymerize, a portion of the monomer will polymerize as a film on the heated mesh. The polymerized monomer will eventually plug the pores on the mesh and adversely effect the delivery of the monomer.

U.S. Patent No. 5,451,260 discloses a system for delivering liquid materials to a reactor using ultrasonic nozzles wherein the liquid monomer is fed by gravity from a storage container to the ultrasonic nozzle via a series of valves. The nozzle then feeds the monomer to the reactor as a mist.

There are several drawbacks associated with the noted system. Most significantly, the amount of liquid monomer delivered to the nozzles is determined by a complex and sequential operation of solenoid valves. The system provides for a delivery tube to be filled with a liquid monomer which is subsequently delivered to the nozzle. Excess liquid monomer is then drained into a storage container.

The noted system further requires precise operation of complex control systems. This is often quite difficult to achieve.

It is also well known in the art that, when employing gravity feed, the amount of liquid delivered to the reactor is proportional to the liquid level in the container. As the liquid level decreases, the static head and the rate at which the liquid drains into the discharge tube are reduced. By relying on timing sequences of valves with a gravity drain, the amount of liquid delivered can, and in many instances will, vary with the level in the reservoir.

Further, the solenoid valves on the noted system are operated by electrical means. During normal operation, the heat generated by the electrical devices increases the temperature of the valve body. Under these circumstances, it has been found that thermally sensitive materials, such as those that polymerize upon exposure to heat, clog the valves. Moreover, solutions wherein the solute crystallizes, present similar problems.

It is therefore an object of the present invention to provide a monomer delivery system for a CVD reactor which supplies a substantially uniform atomized mist at a very precise and controlled rate.

It is a further object of the present invention to provide a monomer delivery system for a CVD reactor which achieves uniform film depositions on all sizes of substrate without the need for expensive or complex structural arrangements.

SUMMARY OF THE INVENTION

In accordance with the present invention, a monomer delivery system for a chemical vapor deposition apparatus is provided, comprising at least one ultrasonic atomizing nozzle disposed in the reactor chamber of the chemical vapor deposition apparatus for supplying a vaporized liquid monomer to the reactor chamber for depositing a film on at least one substrate contained therein, a supply vessel for storing liquid monomer, metering means disposed between the supply vessel and the atomizing nozzle for controlling the amount of liquid monomer delivered to the atomizing nozzle and pulse damping means in communication with said metering means for providing a substantially even flow of liquid monomer to said atomizing nozzle.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and additional advantages and features of the present invention will become apparent from the following detailed description of a preferred embodiment thereof, taken in conjunction with the accompanying drawings, in which:

5 Figure 1 is a schematic diagram of a CVD system constructed in accordance with a preferred embodiment of the present invention; and

Figures 2-5 are schematic diagrams of additional embodiments of the CVD system according to the invention.

10 DETAILED DESCRIPTION OF THE PRESENT INVENTION

The present invention substantially reduces or eliminates all of the problems associated with the prior art. The invention comprises a system and method for delivering
3 complex monomers to RF plasma polymerization reactors using an ultrasonic nozzle and precision fluid metering pumps equipped with a pulse damping devices. The system
15 provides a steady stream of monomer, in the form of a uniform atomized fine mist, to the RF plasma polymerization reactor at a very precise and controlled rate. The precise controls of the invention are particularly important when depositing plasma polymerized films on substrates which commonly move through the plasma region of the RF plasma polymerization reactor, such as a moving film, fabric, or web.

20 Referring to Figure 1, there is shown one embodiment of the ultrasonic nozzle delivery system 10 of the invention, which includes a monomer supply vessel 14, monomer metering means to control the amount of liquid monomer delivered to the ultrasonic nozzle(s) and CVD reactor 40 having a chamber 41 therein. According to the invention, the monomer metering means comprises one or more metering pumps.

25 The reactor chamber 41 can be any type of conventional hot wall or cold wall CVD reactor chamber and is preferably made of stainless steel or a quartz tube. Contained within the reactor is at least one susceptor 43 which supports the substrates 68 to be coated.

The reactor chamber 41 further includes heating means. According to the invention, the heating means comprises one or more electrodes 70. The electrodes 70 are connected to an external power source 71 and are capable of heating the substrates 68 to any desired temperature. A typical range of operating temperatures is from room
5 temperature up to 1200°C.

The monomer supply vessel 14 of the system 10 is adapted to sealably store the liquid monomer. The supply vessel 14 is preferably constructed of stainless steel or other like material.

As illustrated in Figure 1, the monomer supply vessel 14 includes means for
10 maintaining the vessel 14 at a constant temperature. This is preferably achieved by enclosing the sides of the vessel 14 in a electrical heating jacket 16 or a heating jacket through which a heat transfer fluid 18 is circulated.

The monomer supply vessel 14 is also equipped with a transfer tube 20 for
introducing an inert gas. The transfer tube 20 includes a conventional check and needle
15 valves 25, 27. A relief valve 22 is also provided to prevent excessive pressure build up. This feature is provided so that "inert blanketing" of the monomer can be achieved to prevent degradation of monomers that are sensitive to exposure to air or oxygen.

As illustrated in Figure 1, a discharge tube 24 and associated discharge valve 23
are also provided to drain the monomer prior cleaning the vessel 14. The feed tubes 30a,
20 30b, submerged below the liquid level proximate the bottom of the supply vessel 14, facilitate the transfer of the liquid monomer to metering pumps 32a, 32b. By maintaining the open end of the feed tubes 30a, 30b in the range of .5 to 1 in., preferably 1 in., from the bottom wall of the vessel 14, an adequate flow of the monomer to the pumps 32a, 32b is assured.

25 The metering pumps 32a, 32b are preferably positive displacement pumps such as those manufactured by Fluid Metering Incorporated of Oyster Bay, New York. In additional envisioned embodiments, the pumps can comprise conventional gear pumps wherein in the pumping action is created by a pair of gears rotating counter to one another and pumping the fluid entrained in the space between the enmeshed gears. As will be

appreciated by one having skill in the art, various positive displacement pumps capable of self priming and pulling liquid up from a reservoir can be employed within the scope of this invention.

As illustrated in Figure 1, the metering pumps 32a, 32b are connected to ultrasonic
5 nozzles 36a, 36b proximate the discharge ends 35a, 35b of the delivery tubes 30a, 30b. The nozzles 36a, 36b are of conventional construction, and by way of example can be of a type manufactured by Sono-Tek, Milton, New York.

The ultrasonic nozzles 36a, 36b are connected to the reactor chamber 40 and preferably deliver the monomer mist directly to the reactor chamber 41. In additional
10 envisioned embodiments (not shown), the monomer mist is delivered to a distant location inside the reactor via a delivery tube. In a preferred embodiment, direct discharge of the atomized mist is employed.

According to a preferred embodiment of the invention, the liquid monomer from positive displacement pump 32a is directly fed to a respective ultrasonic nozzle 36a. A
15 separate pump 32b and nozzle 36b combination is employed to deliver the atomized mist to a different position in the reactor chamber 41.

By feeding monomers to different locations within the reactor 40 with a series of pump-nozzle sets (while targeting the delivery to the space between the RF electrodes), a uniform distribution of monomers can be assured when depositing on substrates 68 that
20 cover a large surface area. In this manner the deposition of a uniform film thickness over the entire surface of large surface area substrates 68 is assured.

A key feature of the present invention is the pulse damping means which provides a substantially even flow of liquid monomer at a substantially constant pressure to each nozzle 36a, 36b. According to the invention, the pulse damping means can be an integral
25 feature of metering pumps 32a, 32b or separate components (not shown).

The pulse damping means of the invention are designed and adapted to smooth out the pressure variations inherent in the discharge of positive displacement pumps. In a preferred embodiment, the pulse damping means comprises a conventional pulse damper such as that manufactured by Fluid Metering Incorporated, Oyster Bay, New York.

Applicant has specifically found that a unique synergism is achieved between the metering means (i.e., pumps 32a, 32b) and pulse damping means of the invention. This unique synergism provides for a precisely controlled, substantially uniform flow of liquid monomer to and through the ultrasonic nozzles. As a result, substantially uniform CVD
5 films can be achieved on a variety of stationary and moving substrates.

In a preferred embodiment, illustrated in Figure 1, the ultrasonic nozzles are affixed to a side of the reactor 40 such that the ultrasonic nozzle tips 37, 38 direct vaporized liquid monomer in a substantially horizontal direction toward the substrates 68 to be coated. As will be appreciated by one having ordinary skill in the art, any number
10 (e.g., from 1 to 6) of the ultrasonic nozzles 36a, 36b can be employed within the scope of the invention. The use of multiple nozzles permits the formation of complex films on a multitude of substrate shapes and orientations.

As illustrated in Figure 1, a conventional microprocessor 60 can be employed to control the delivery system, including the supply vessel valves 22, 25, 27, metering
15 pumps 32a, 32b and nozzles 36a, 36b. The microprocessor 60 can also be adapted to control operation of the reactor chamber electrodes 70, vacuum pump 45 and associated exhaust valve 44.

In an additional embodiment of the invention, illustrated in Figure 2, a single pump 38 is employed to feed a set of ultrasonic nozzles 39a, 39b via line supply line 33.
20 The manifold 50 is provided with supply valves 51a, 51b, to assure that an equal amount of liquid monomer is being delivered to each nozzle 39a, 39b. According to the invention, various pump/nozzle combinations can be employed to deliver different fluids to the reactor at the same time or in a programmed sequence.

When delivering different materials at the same time, components can be mixed in
25 the liquid phase and delivered as a single fluid. This method eliminates the need for mixing and delivers a uniform composition of the mixture to the reactor. As illustrated in Figures 3 through 5, a series of ultrasonic nozzles may be employed (or a single unit) which are placed in such a manner that when depositing plasma polymerized films on to films, fabrics or webs, there is a uniform distribution of monomer mist being transported
30 through the plasma deposition zone.

To improve deposition efficiency, it is preferred that the monomer mist or aerosol be fed into the zone 69 that is encompassed by the electrodes 70 of the RF plasma polymerization reactor 40 such that the monomer mist or aerosol is fed directly into the RF field and the zone 69 where the substrate 68 to be coated is located. By feeding the monomer mist or aerosol in this manner, the ionization of the monomer and deposition of the desired film on the substrate 70 will be assured (see Figure 3). According to the invention, the electrodes 70 in the reactor and the substrates 68 can be arranged in any orientation in 360° space since the mist will be delivered to the substrate regardless of its orientation.

Referring now to Figure 4, by way of example, electrode 75 is curved to follow the contour of a drum 72 which transports a continuous web type substrate 73 on its surface. By directing the monomer mist (via nozzles 50a, 50b) into the space between the electrode 75 and the substrate 73 at the locations shown, a uniform coating of the substrate is assured. This example illustrates a completely different and novel orientation of the electrode 75 and substrate 73.

In yet another embodiment of the invention, illustrated in Figure 5, a continuous fabric or web type substrate 74 is transported through a festoon type arrangement of rollers 80. The continuous web type substrate 74 is transported between electrodes 78 and baffles 79. The ultrasonic delivery nozzles 81 are disposed proximate the rear wall of the reactor 40 such that the monomer mist is directed into the space between the electrodes 78 and, thus, into the ionization zone 90.

The system described herein is designed to assure a uniform distribution of the monomer into the ionization zone and thus the zone of film deposition. It will be apparent to those skilled in the art that there are several possible approaches that can be used to orient the substrate, electrodes and the delivery of the monomer mist depending on the specific requirements of the plasma deposition system.

The features and advantages of the present invention are more fully shown with respect to the following examples. The examples are for illustrative purposes only and are not meant to limit the scope of the claims in any way.

The components used in the following examples are a Model 8700-120MS MICROSPRAY[®] Nozzle manufactured by Sono-Tek, Milton, New York 12547, and a Model RHSY1CKC pump equipped with a PD-60-LF pulse damper, manufactured by Fluid Metering Incorporated, Oyster Bay, New York 11771.

5 Example 1

The monomer 2-Hydroxyethylmethacrylate, with the chemical formula $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{OH}$, has a molecular weight of 130 and has a normal boiling point of 208°C. The vapor pressure of this monomer is so low at temperatures much below its boiling point that even when inert gas is bubbled through a container of this material, insufficient monomer is delivered to a process vessel such a plasma polymerization reactor. This materials is also thermally sensitive and autopolymerizes into a high molecular weight gel when heated to temperatures above 60°C. Thus, heating the monomer to increase its vapor pressure is not possible. It is also impossible to deliver any significant quantity of this monomer to a plasma polymerization reactor using

10
15⁹ conventional methods.

In this example, 2-Hydroxyethylmethacrylate was delivered to a 4.0 liter plasma reactor with internal electrodes spaced 2.0 inches apart and driven by a 200 watt RF generator operating at 13.56 Mhz. The reaction chamber was connected to an Alcatel 2020 CP vacuum pump with a pumping capacity of 16 cfm. A manual throttle valve was

20 employed to control the reaction chamber pressure independent of the monomer flow.

The monomer, which is a liquid at room temperature, was placed in an 150 ml round bottom flask equipped with a stopper through which a 1/4" tubing had been inserted. The flask was filled to the 50% level with the monomer. The other end of the tubing was connected to the suction side of the displacement pump. The output of the pump was fed directly to the feed port of the ultrasonic nozzle. The nozzle was mounted directly on the reaction chamber such that the mist is directed between the electrodes, as illustrated in Figure 3.

25

Since the reactor used in this example had a small volume, a single nozzle was adequate for directing the mist towards the vertically oriented substrate in sufficient

quantity and in a uniform manner. A silicone tubing was placed equidistant from the two electrodes and secured on a plastic fixture located at the base of the reactor. The stroke setting on the pump was set for 300 strokes per minute which delivers the monomer at a rate of 30 cc/min. The liquid was atomized by the ultrasonic nozzle and at this flow rate
5 the reactor is maintained at a pressure of 300 mTorr. RF power is set at 120 watts for a period of five (5) minutes.

At the end of the deposition process, the tubing was removed and examined for evidence of a plasma deposited film. The presence of the plasma polymerized film was detected by the change in the color of the tubing from its natural clear state to one having
10 a coating with a very visible amber color. The presence of a substantial thickness of coating was determined by staining the coated tubing with Congo Red. A very intense red color was developed on the surface of the coating and this color did not wash away indicating the coating was firmly adhered on the surface.

Example 2

15 The monomer 1,6-hexanediamine is a difunctional amine monomer, with a six carbon spacer, and offers an opportunity to deposit amine functional films where the amine group is spaced a sufficient distance from the surface of the substrate to enhance their reactivity. This monomer is, however, a solid at room temperature having a melting point of 42°C, is very corrosive, and has a high boiling point of 204°C. Feeding this
20 monomer into a plasma reactor poses several problems. For example, if an inert gas is used to bubble through the heated liquid, the amount of monomer delivered to the reactor is insufficient to allow deposition of a thick enough film with the requisite functional density. In fact, the density of functional groups is less than 0.1 nmoles/cm². This is because much of the reactor pressure is derived from the presence of high concentration
25 of the inert carrier gas rather than the monomer itself. An additional problem that is encountered is the cooling of the vapor in the delivery tube and subsequent blockage due to solidification of this cooled and liquefied vapor in the delivery tube.

In this example, the noted monomer was mixed with less than 10% of another amine monomer, such as ethylene diamine which serves to maintain the mixture in a

liquid state. This mixture was then delivered to a plasma polymerization reactor using the ultrasonic nozzle system illustrated in Figure 3.

The plasma reactor was a 4.0 liter cylindrical vessel with internal electrodes spaced 2.0 inches apart and driven by a 200 watt RF generator operating at 13.56 Mhz.

- 5 The reaction chamber was connected to an Alcatel 2020 CP vacuum pump with a pumping capacity of 16 cfm. A manual throttle valve was employed to control the reaction chamber pressure independent of the monomer flow.

- 10 The monomer mixture, which is a liquid at room temperature was placed in an 150 ml round bottom flask equipped with a stopper through which a 1/4" tubing has been inserted. The flask was filled to the 50% level with the monomer. The other end of the tubing was connected to the suction side of the pump. The output of the pump was fed directly to the feed port of the ultrasonic nozzle. The nozzle was mounted directly on the reaction chamber such that the mist is directed between the electrodes (as shown in Figure 3) except that the mist was directed in a plane parallel to the plane in which the substrate
15 to be coated is located.

- Since the reactor used in this example had a small volume, a single nozzle was adequate for directing the mist towards petri dishes containing 120 μm polystyrene beads. The petri dishes containing the beads were placed on top of a plastic bar placed horizontally at the bottom of the reactor chamber. Instead of the flow being vertically
20 directed as shown on Figure 3, the mist was directed horizontally into the chamber above the petri dishes containing the polystyrene beads. The stroke setting on the pump was set for 600 strokes per minute which delivers the monomer at a rate of 60 cc/min. The liquid was atomized by the ultrasonic nozzle and at this flow rate the reactor is maintained at a pressure of 450 mTorr. RF power is set at 90 watts for a period of three (3) beads were
25 removed from the reactor. The beads were washed in methanol and tested for the presence of amine functional groups on the surface. Chemical analysis using a ninhydrin assay for primary amines showed a concentration of 1.15 $\mu\text{moles/gm}$. Since the beads have a surface area of 309 cm^2/gm , this equates to a surface functional density of 3.7 nmoles/cm^2 .

From these examples, it will be apparent to those skilled in the art that many possible electrode orientations, substrates and nozzle locations (such as that illustrated in Figures 1 through Figure 5), can be employed to deposit plasma enhanced CVD films on a variety of stationary and moving substrates. Further, both single monomers and
5 mixtures of monomers can be delivered to plasma polymerization reactors for the purpose of depositing plasma enhanced CVD films on a variety of substrates using the methods described in this invention.

While the invention has been described with reference to specific aspects, features, and embodiments thereof, it will be apparent that various modifications, variations and
10 embodiments are possible, and accordingly the invention is to be broadly construed with respect to all such modifications, variations and embodiments, as being within the spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A monomer delivery system for a chemical vapor deposition apparatus, comprising:

at least one ultrasonic atomizing nozzle disposed in a reactor chamber of said
5 chemical vapor deposition apparatus for supplying a vaporized liquid monomer to said reactor chamber for depositing a film on at least one substrate contained therein;

a supply vessel for storing said liquid monomer, said supply vessel including means for heating said vessel;

metering means disposed between said supply vessel and said atomizing nozzle
10 and in communication therewith for controlling the amount of liquid monomer delivered to said atomizing nozzle; and

pulse damping means in communication with said metering means for providing a substantially even flow of liquid monomer at a substantially constant pressure to said atomizing nozzle.

15 2. The monomer delivery system of Claim 1, wherein said vaporized liquid monomer is delivered to said reactor chamber at a rate in the range of approximately 3.5 to 60 cc/min.

3. The monomer delivery system of Claim 1, wherein said heating means includes means includes means for maintaining said vessel at a substantially constant temperature.

20 4. The monomer delivery system of Claim 1, wherein said metering means comprises a positive displacement pump.

5. The monomer delivery system of Claim 1, wherein said damping means comprises a pulse damper.

6. The monomer delivery system of Claim 1, further comprising at least a second ultrasonic atomizing nozzle and at least a second metering means for controlling the amount of liquid monomer delivered to said second ultrasonic atomizing nozzle for vaporization and injection into said reactor chamber.

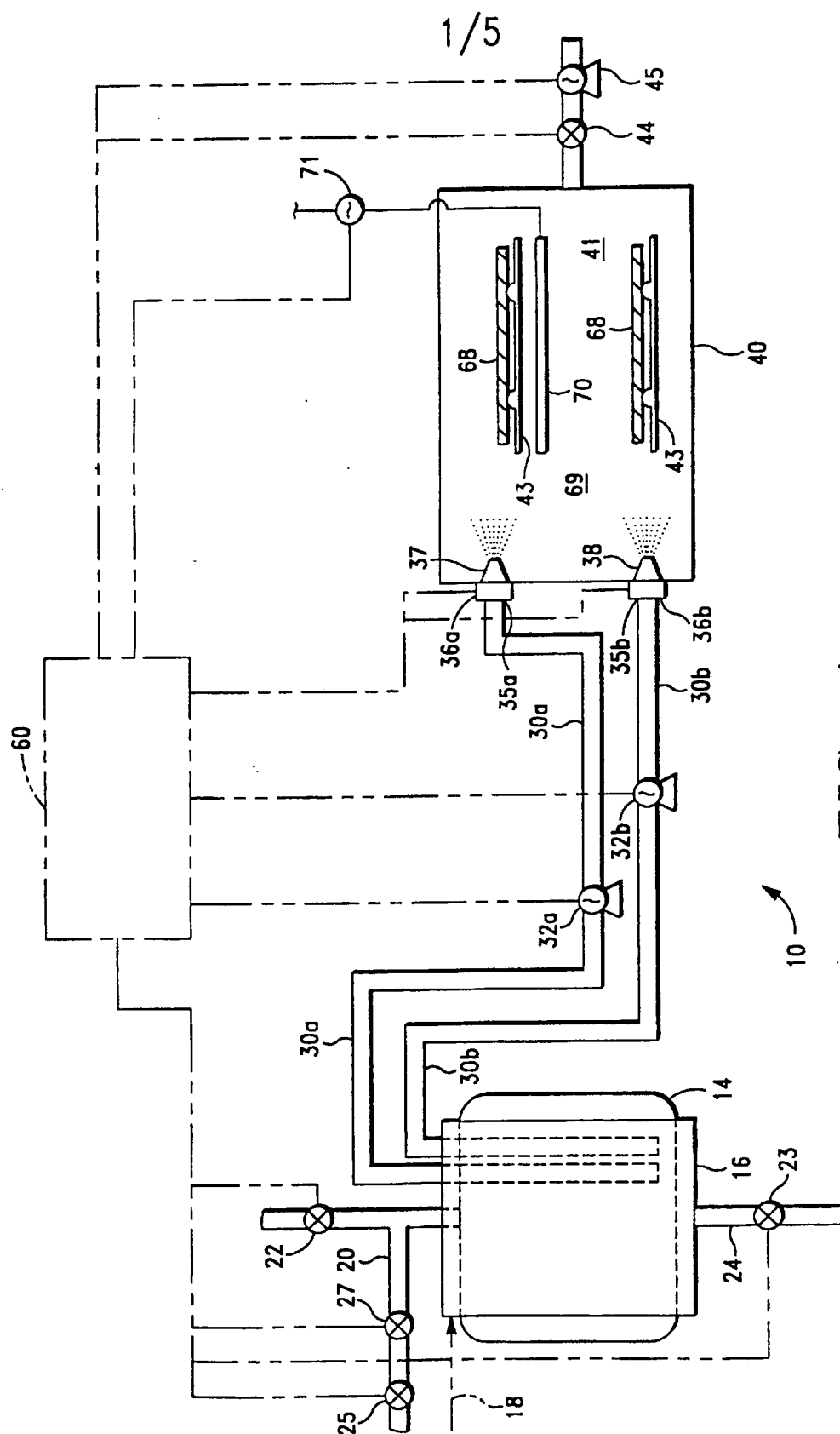


FIG.-1

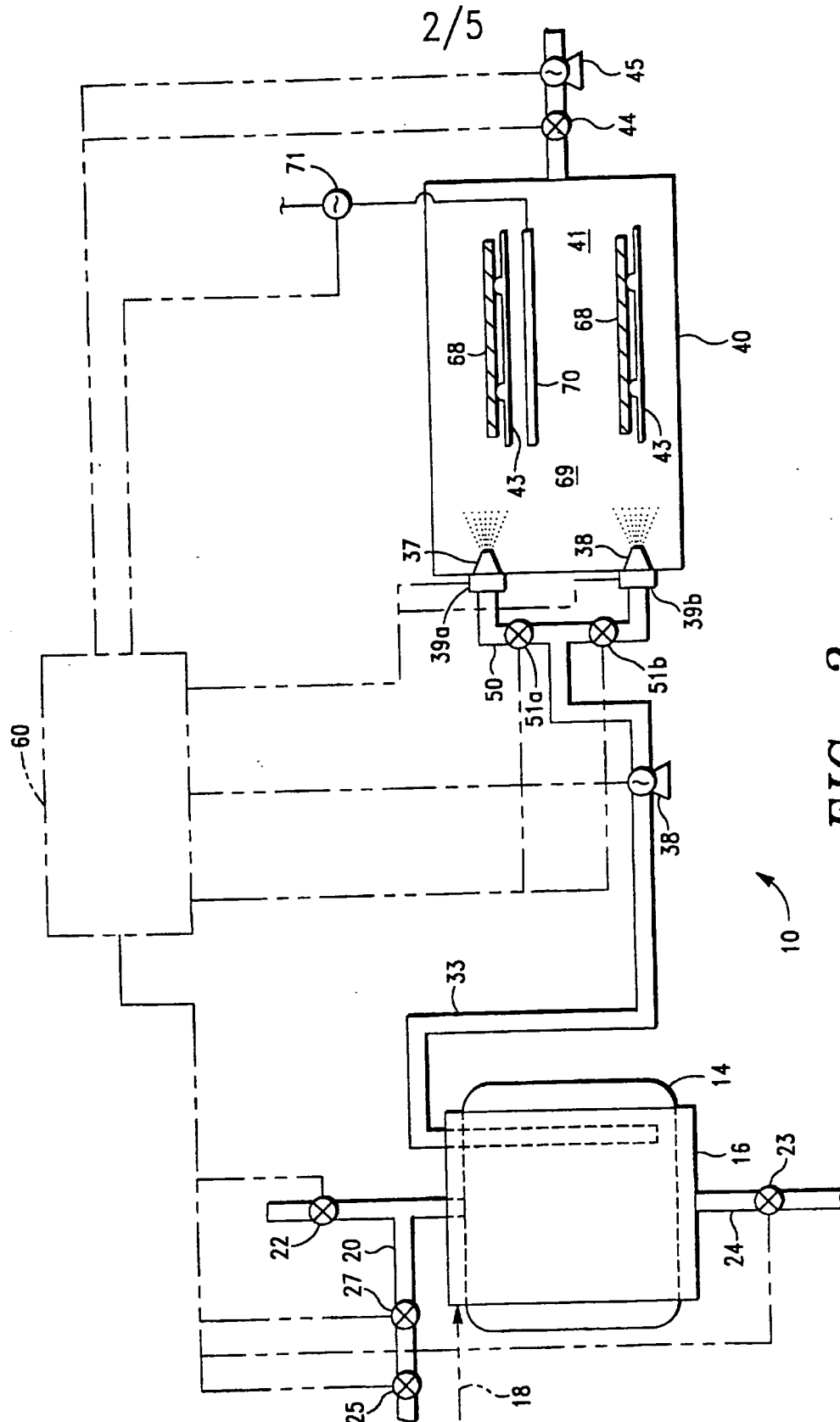


FIG. -2

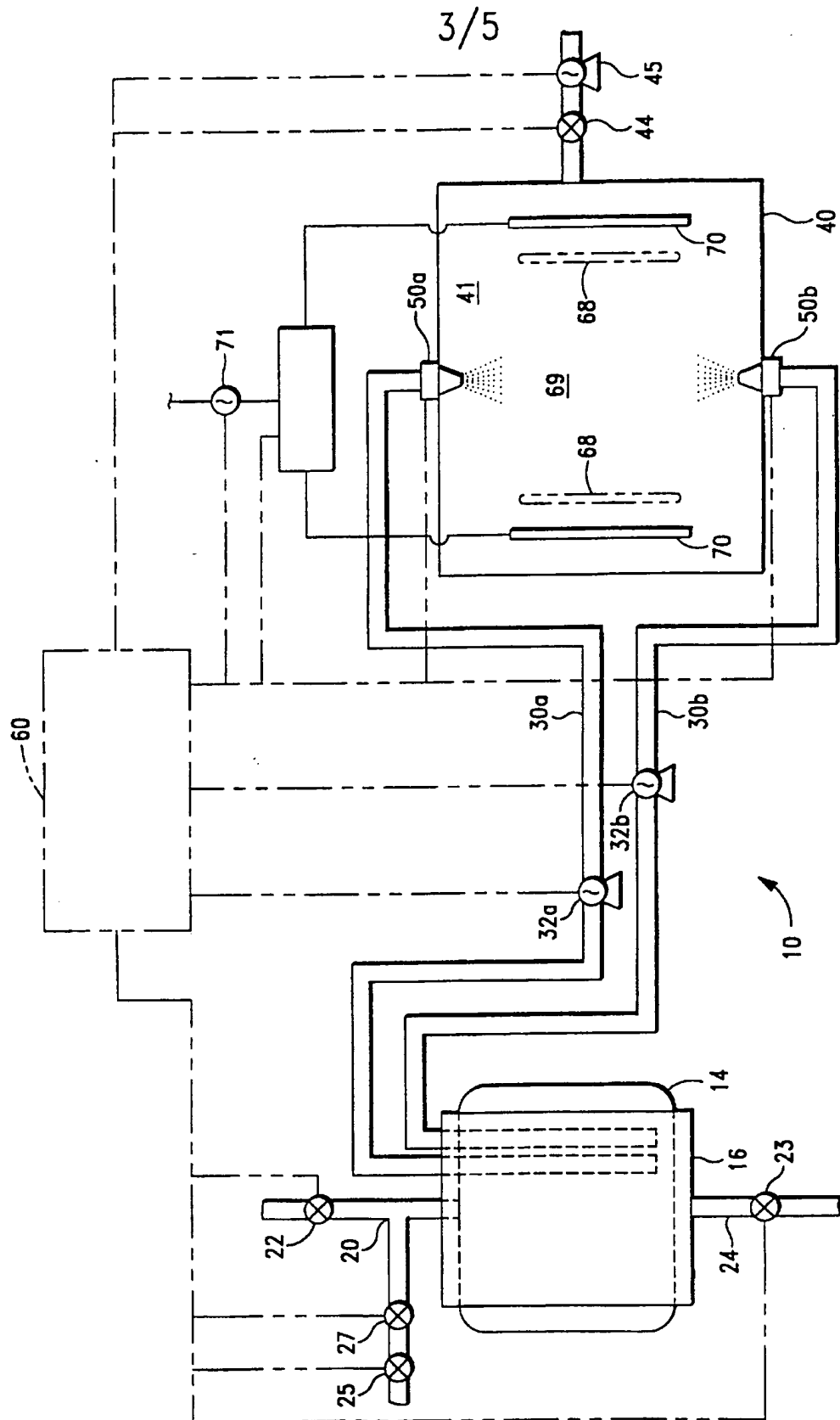


FIG. -3

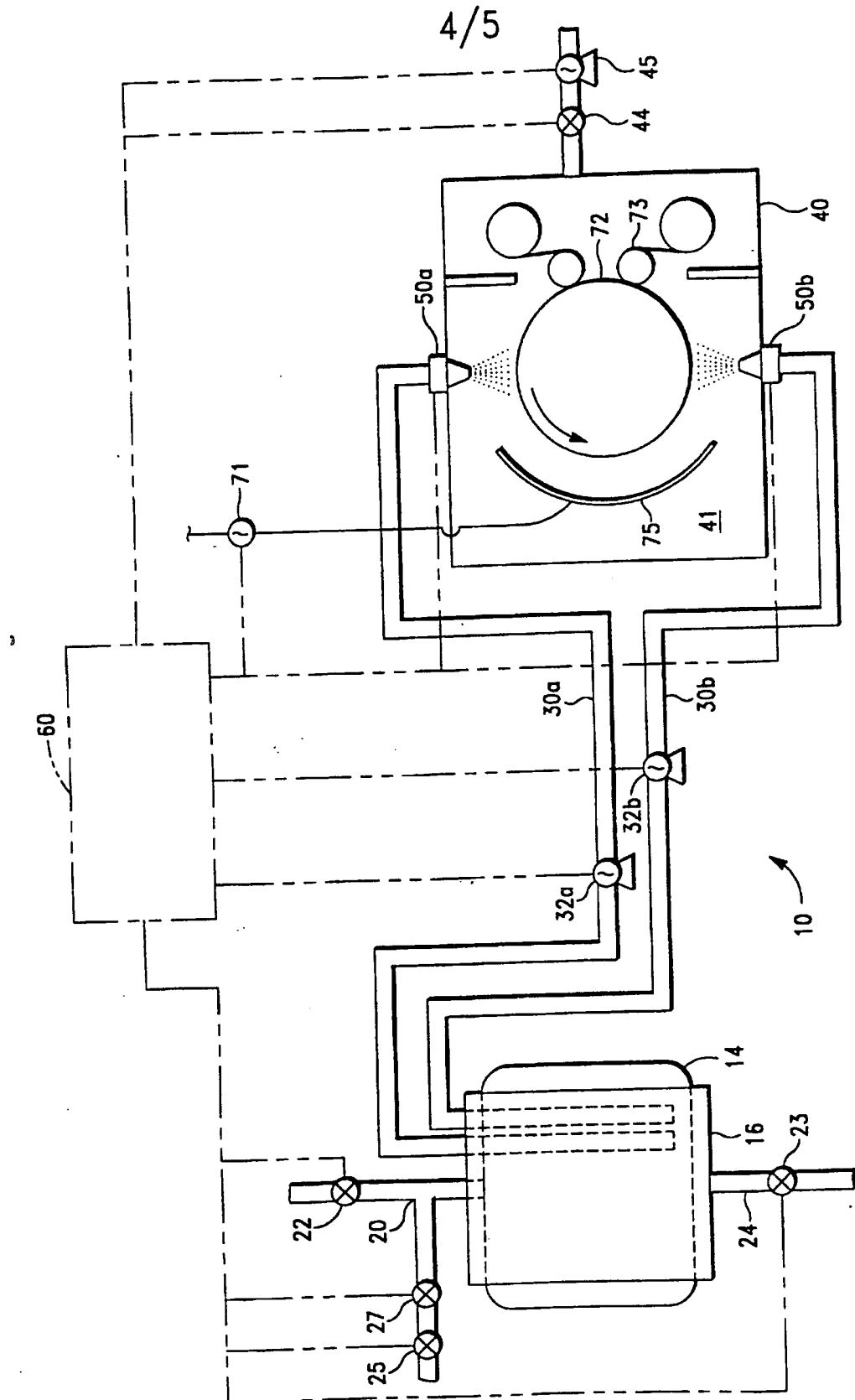


FIG. 4

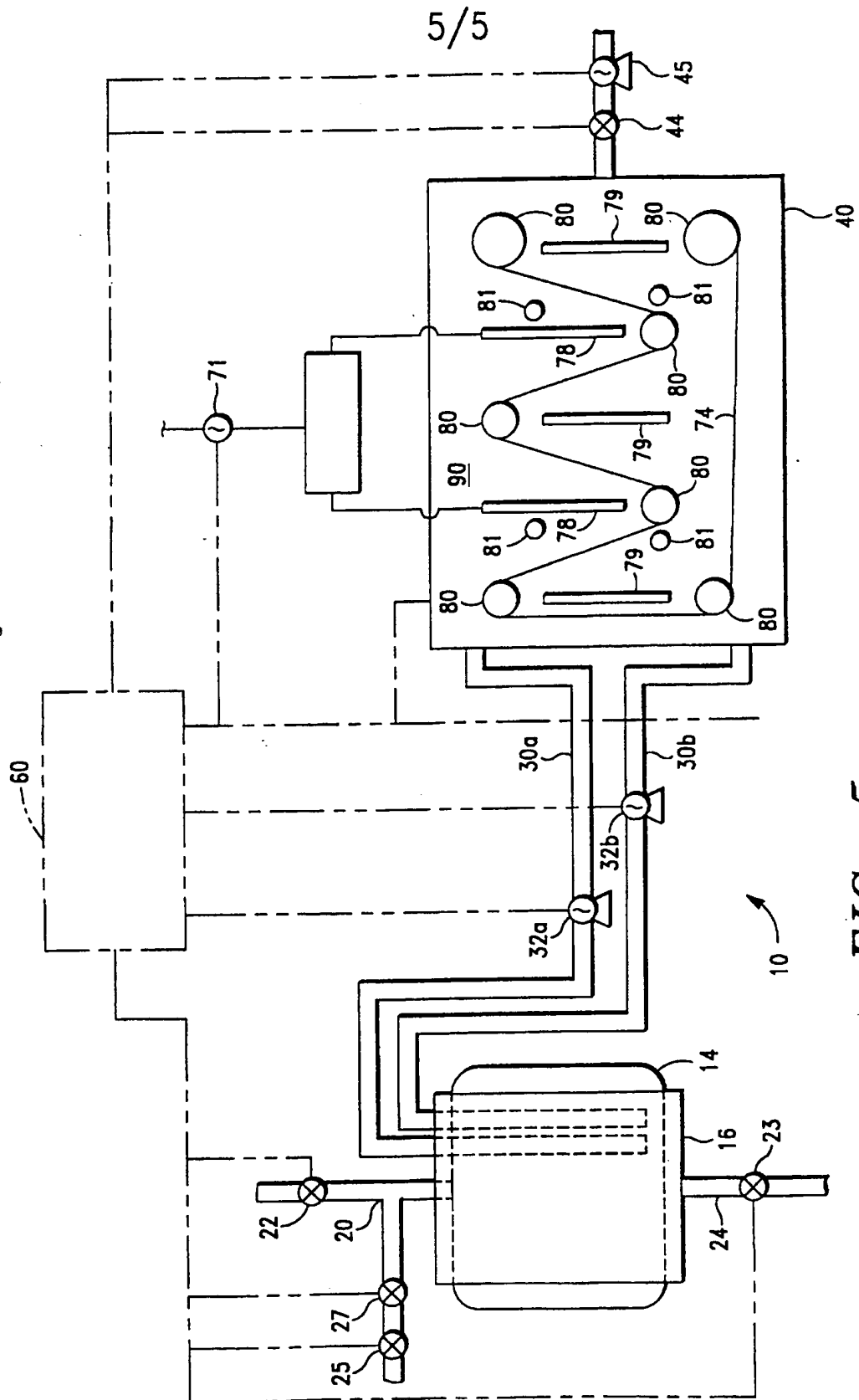


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US97/15806

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C23C 16/00

US CL : 118/715, 726

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 118/715, 726; 427/421, 424

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS search

search terms: atomiz?, ultrasonic, nozzle, monomer, meter?, pulse, damp?

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US 5,620,524 A (FAN ET AL) 15 April 1997; abstract, column 5-line 5 to column 6-line 21; column 11-line 52 to column 15 -line 20; figures 1-2 and 4.	1-6
Y ,	US 5,451,260 A (VERSTEEG ET AL) 19 September 1995, column 3, lines 3-46, and figure 1.	1, 6
Y	US 5,322,710 A (VISSER) 21 June 1994, column 4, lines 23-42, and figure 1.	1, 3
Y	US 4,640,221 A (BARBEE ET AL) 03 February 1987, column 2, lines 45-54, and figure 1.	1, 3
Y	US 5,462,014 A (AWAYA ET AL) 31 October 1995, column 7, lines 13-30, and figures 2A and 2B.	1, 3



Further documents are listed in the continuation of Box C.



See patent family annex.

*

Special categories of cited documents:

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US 5,609,897 A (CHANDLER ET AL) 11 MARCH 1997, column 8, lines 25-27.	1, 5
A	US 4,529,427 A (FRENCH) 16 JULY 1985, column 2-line 54 to column 3-line 36, figure 2.	1, 6

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